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PM2.5/SOP-4
REVISION HISTORY

| Rev. | Responsible Official | Date |
|-------------|-----------------------------|-------------|
| 0 | Steve Taylor | 2001-10-01 |
| 1 | Steve Taylor | 2002-11-01 |

1.0 PURPOSE

1.1 This document describes the procedures used at the National Air and Radiation Environmental Laboratory (NAREL) for the determination of organic (OC), elemental (EC), carbonate (CC), OCX and total carbon (TC) in PM_{2.5} particulate matter collected on quartz fiber filters using a thermal/optical carbon analyzer.

2.0 SCOPE AND APPLICATION

2.1 This procedure provides detailed instructions for sample preparation and analysis of quartz fiber filters using a Sunset Laboratory thermo-optical transmittance (TOT) carbon analyzer. Procedures for sample inspection, measurement, calculation, documentation, archival, safety, and quality control are included.

2.2 This method is restricted for use by or under the supervision of analysts trained in the operation of the Sunset Laboratory TOT Carbon analyzer. Each analyst must demonstrate the ability to generate acceptable results with this method.

3.0 DEFINITIONS

3.1 Organic Carbon (OC) - Optically transparent carbon removed (through thermal desorption or pyrolysis) when heating a filter sample to a preset maximum (900°C) in a non-oxidizing (helium) carrier gas.

3.2 Elemental Carbon (EC) - Optically absorbing carbon (e.g., in soot particle cores) that can only be removed from the filter by thermal evolution under an oxidizing carrier gas (He/O₂).

3.3 Carbonate Carbon (CC) - Carbonate Carbon (CC) - Inorganic carbon that thermally decomposes to carbon dioxide. Calcium carbonate decomposes at 825°C.

3.4 Total Carbon (TC) - The summation of the organic, elemental, and the carbonate carbon observed on the filter.

3.5 OCX - The organic carbon evolved between 550°C and the addition of oxygen. The start integration times for the fourth OC peak is optimized to begin integration at 550°C. OCX is used to adjust the OC and EC data when comparing to data analyzed by the Interagency Monitoring of Protected Visual Environments (IMPROVE) TOR method.

3.6 Pyrolyzed Carbon – Light absorbing carbon (char) formed in the organic carbon portion of the analyses by incomplete combustion of OC. This is corrected by the laser transmission which defines a split point between the organic and elemental fractions.

3.7 Split point or split time – The transmittance of the analyzer's laser through the filter decreases as pyrolytically formed carbon (char) is produced. The light transmittance increases as the char and original EC are removed during the oxidizing stage of analysis.

The split point is the time during the analysis in which the laser transmittance matches the initial transmittance measured at the beginning of the analysis plus the transit time.

3.8 TOT - Thermal/Optical Transmittance

3.9 TOR - Thermal/Optical Reflectance

3.10 LABORATORY DUPLICATES - Two filter punches taken from the same sample filter and analyzed separately with identical procedures. Analyses of laboratory duplicates indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures

3.11 FIELD DUPLICATES - Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

3.12 Instrument Blank - A quartz filter punch that was pre cleaned in the instrument's oven and analyzed as a sample. This filter is not exposed to the room's atmosphere. The instrument blank is used as a check of the instrument's baseline.

3.13 Method Blank - A quartz filter punch that was pre cleaned, spiked with any reagents used in the method and analyzed exactly as a sample. The method blank is used to determine if method interferences are present in the laboratory environment, the reagents, or the apparatus

3.14 ICV - Instrument calibration verification standard. An independent standard that is derived from a second source.

3.15 CCV - Continuing Calibration Verification. A quality control check standard which is analyzed periodically to test the accuracy of the measurement system.

3.16 COC - Chain Of Custody. An unbroken trail of accountability that ensures the physical security of samples, data, and records.

3.17 I.S. - Internal Standard. A component (5% methane in helium) injected into the instrument through a fixed volume loop near the end of each analysis to provide a relative response factor for data reduction.

3.18 LCS - Laboratory Control Sample. A quality control sample that contains spiked analytes which is prepared and analyzed along with each sample batch.

3.19 MASB - Monitoring and Analytical Services Branch. The branch at NAREL is responsible for the analysis of environmental samples for radioactive and/or mixed waste contamination.

3.20 NAREL - National Air and Radiation Environmental Laboratory.

3.21 NIST - National Institute of Standards and Technology.

3.22 PM_{2.5} - Particulate Matter with an aerodynamic diameter less than or equal to 2.5 micrometers.

3.23 QAC - Quality Assurance Coordinator. The person with primary responsibility for

overseeing the NAREL QA/QC Program.

3.24 RTI - Research Triangle Institute, the independent contractor laboratory for the PM_{2.5} Chemical Speciation Program.

3.25 SHEM - Safety Health and Environmental Management

3.26 SOP - Standard Operating Procedure. The officially approved document that describes in detail the steps of a procedure for performing a routine or repetitive task.

3.27 LIMS - Laboratory information management system.

3.28 Transit Time - The time in seconds that it takes for the carrier gas to transfer the evolved carbon from the sample to the FID.

4.0 SUMMARY OF METHOD

4.1 This procedure is a thermal-optical transmittance (TOT) method based on NIOSH method 5040. This method uses thermal desorption in combination with optical transmission of laser light through the sample to speciate carbon collected on a quartz fiber filter. A precision tool is used to punch out a section from an aerosol sample previously collected on a quartz fiber filter. The filter section (punch) is placed into the instrument's quartz oven and purged with helium. The oven's temperature is increased in ramped steps up to 900 °C. Helium purges the thermally removed organic carbon and pyrolysis products into a manganese dioxide oxidizing oven where they are converted to carbon dioxide gas. The CO₂ gas is then mixed with H₂ and carried by the helium through a heated nickel catalyst which converts the CO₂ into methane (CH₄). The methane is subsequently measured using a flame ionization detector (FID). The instrument's quartz oven is then cooled to 600°C and the carrier gas is switched to a helium/oxygen mixture and a second temperature ramp is initialized. Elemental carbon is oxidized off the sample punch and carried through the system and measured in the same manner as the organic carbon. Both external (sucrose solution) and internal (methane) carbon standards are used for FID calibration.

Elemental carbon can be formed by pyrolysis (charring) of organic carbon during the initial non-oxidizing temperature ramp. An artificially low organic carbon and high elemental carbon measurement results. Because elemental carbon is a strong absorber of light, pyrolysis products formed on the quartz filter punch will cause a decrease in light transmission through it. To correct for error produced from pyrolysis products a laser is used to determine a split point that separates the elemental carbon formed by charring from the elemental carbon that was originally in the sample. This is done by focusing a laser beam through the filter punch while it is being analyzed. If pyrolysis products form during the non-oxidizing stage of analysis, the light transmission monitored through the filter will decrease. During the second or oxidizing stage of analysis, pyrolysis products and elemental carbon originally on the punch will be burned off and light transmission through the punch will increase to background levels for a clean quartz punch. The split point separating elemental carbon formed by pyrolysis from original elemental carbon is the point in time during the analysis at which the laser signal measured during the oxidizing stage equals the initial laser signal.

5.0 Safety

5.1 All procedures performed at NAREL must be conducted following the requirements detailed in the *NAREL Chemical Hygiene Plan* and the *NAREL Radiation Safety Manual*.

5.2 All NAREL laboratory personnel are expected to use good laboratory practices. Most of the safety training is provided by the SHEM officer. All lab personnel are expected to conform to directives given by the SHEM officer.

5.3 The Sunset Laboratory Thermal/Optical Carbon Analyser uses high temperatures (up to 900 C) and laser radiation to perform the required steps in this analytical procedure. Under normal operation, the analyst is protected from exposure to these energy sources. However, during repair or trouble shooting, when the instrument cover is removed, the analyst must take the following precautions.

5.4 Before attempting any repairs, turn off the power and wait for all heated zones to cool.

5.5 For most repair work, unplug power to the ovens and avoid contact with any power sources in the oven cabinet.

5.6 Do not look directly at the laser source as permanent eye damage can occur.

5.7 Use caution when handling all support gas cylinders and regulators. Always have cylinders properly chained to a safety rack.

6.0 INTERFERENCES

6.1 High levels of carbonate carbon will interfere with the organic carbon. Samples above 5% carbonate present significant interference. Samples that are colored after the analyses indicate significant inorganic material (soil).

6.2 Samples that are optically too dark such as those with high mineral deposit or carbon levels will interfere with the laser transmission and automatic split point.

6.3 High mineral deposits will act as a catalyst to oxidize the organic carbon at a lower temperature.

6.4 Samples that are very heavily loaded with EC will interfere with the automatic split point.

7.0 EQUIPMENT AND SUPPLIES

- 7.1 Sunset Labs Thermal/Optical Carbon Analyzer
- 7.2 Precision Punch 1.5 cm²
- 7.3 Syringes: 10 uL and 25 uL or Eppendorf 10 uL pipettor
- 7.4 Tweezers
- 7.5 Petri dishes 50 mm diameter with tight fitting lid
- 7.6 Helium purifiers: Supelco heated high capacity gas purifier, catalog # 23800
Restek indicating oxygen trap, catalog # 22010
- 7.7 Volumetric Flasks, Class A
- 7.8 Analytical Balance, capable of weighing to ± 0.0001 g.
- 7.9 Regulators for gas cylinders.
- 7.10 Box Furnace (Lindburg/Blue M No. BF51732PBC or equivalent).
- 7.11 Crucible or ceramic dish (To contain filters when in furnace)
- 7.12 Quartz filters (Whatman Catalog No. 1851047, grade QMA or equivalent)

8.0 Reagents and Gases

- 8.1 Helium - At least 99.999 ultra high purity grade with low moisture, hydrocarbon and oxygen background.
- 8.2 Air - Ultra zero grade with low moisture and hydrocarbon background.
- 8.3 Hydrogen - 99.997% high purity or better. (Hydrogen generator)
- 8.4 Helium/Oxygen - This is a custom blend gas with 10% oxygen with a helium balance. It should be ordered with sufficient lead-time to allow for blending by the gas vendor (typically 3 - 4 weeks). The helium should be the same quality as the main source helium and the oxygen should be 99.999% or better with low moisture, hydrocarbon background and CO₂ (< 1 ppm).
- 8.5 Helium/methane - This is also a custom blend with 5.0% methane with a helium balance. Again, this should be ordered with sufficient lead-time to allow for blending by the gas vendor (typically 2 - 4 weeks). The helium should be the same quality as the main source helium and the methane should be research grade or better with low moisture background.
- 8.6 Nitrogen - Purified
- 8.7 Sucrose - Certified ACS Fisher Cat. No. S5-500 or equivalent.

- 8.8 Potassium Hydrogen Phthalate (KHP) Primary standard grade Fisher P243 or equivalent.
- 8.9 Organic-free water - Generated in house with Barnstead unit.
- 8.10 Hydrochloric Acid (HCl) 37% ACS Reagent Grade or equivalent.
- 8.11 Calcium Carbonate - ACS Reagent Grade or equivalent.

9.0 Standards Preparation

9.1 Stock Sucrose Solution - Dissolve 9.500 g of sucrose in reagent grade water and dilute to 100 ml. This solution has a concentration of 40.0 ugC/uL.

$$\left(\frac{9.500 \text{ g Sucrose}}{100 \text{ ml}}\right) \left(\frac{144.12 \text{ g Carbon}}{342.31 \text{ g Sucrose}}\right) \left(\frac{10^{-3} \text{ ml}}{\text{uL}}\right) \left(\frac{10^6 \text{ ug}}{\text{g}}\right) = 40.0 \text{ ugC / uL solution}$$

9.2 Instrument calibration verification solution (ICV) - Dry the KHP at 110°C for two hours. Allow to equilibrate to room temperature. Dissolve 0.3826 g of KHP in reagent grade water with 0.4 ml concentrated HCL and dilute to volume in a 100 ml volumetric flask. The concentration is 1.80 ugC/uL of solution.

$$\left(\frac{0.3826 \text{ g KHP}}{100 \text{ ml}}\right) \left(\frac{96.08 \text{ g Carbon}}{204.23 \text{ g KHP}}\right) \left(\frac{10^{-3} \text{ ml}}{\text{uL}}\right) \left(\frac{10^6 \text{ ug}}{\text{g}}\right) = 1.80 \text{ ugC / uL solution}$$

9.3 Calibration standards -Prepare at least three calibration standards that span the measurement range of the samples by diluting aliquots of the stock sucrose solution with reagent water.

| | Sucrose Stock (ugC/uL) | Volume of Stock (ml) | Volume Final (ml) | Final Concentration ugC/uL) |
|-------|------------------------|----------------------|-------------------|-----------------------------|
| Std 1 | 40.0 | 1.0 | 100.0 | 0.40 |
| Std 2 | 40.0 | 5.0 | 100.0 | 2.00 |
| Std 3 | 40.0 | 10.0 | 100.0 | 4.00 |

10.0 Quartz Filter Preparation

10.1 Place 50 - 100 filters in a crucible or ceramic dish and heat in a box furnace for at least 3 hours at 900 °C. After heating, allow the filters to cool in the furnace under a low flow of nitrogen. Select 2 filters at random and analyze as detailed in Section 16. Total carbon must be less than 1.0 ug/cm² for the batch of filters to be acceptable. Assign the filters a batch number. Batches of acceptance tested filters are placed in groups of 8-10 in new petri dishes with tight fit lids and labeled with the batch number. The petri dishes with filters are placed in resealable plastic bags and stored in a freezer until used.

10.2 Naming Quartz Filters - Quartz filters are given an identification number when they are needed for a specific project. The naming convention for quartz filters is as follows: Q + year + sequence number. For example Q01-100121. The next sequence number is found in the PM_{2.5} LIMS. Each filter is placed in an individual petri dish with tight-fit lid labeled with the unique identification number.

11.0 SAMPLE COLLECTION, PRESERVATION, AND ARCHIVAL

11.1 Samples that are shipped to or from NAREL will be in individual petri dishes with tight-fit lids, placed in an insulated cooler containing blue ice to maintain a temperature ≤ 4 °C.

11.2 Samples are logged into the PM_{2.5} LIMS and given an identification number.

11.3 Samples are stored in their petri dishes in the PM_{2.5} freezer until time of analysis.

11.4 Samples to be archived are kept in their original petri dishes sealed in zip lock bags and stored in the PM_{2.5} freezer.

12.0 Work Area Preparation

12.1 The work area for preparing filter punches should be free of dust and chemicals. Cover the area with 5 - 6 layers of aluminum foil. Tape the edges down to secure the foil to the counter top.

12.2 Clean an area of about 2 inches square on the foil. Use a new, clean quartz filter rolled around the tip of forceps to scrub the foil clean. This cleaned area will be used when cutting filter punches.

13.0 Analyzer Start-Up

13.1 Ensure that the gas cylinders have at least 200 - 300 psi.

13.2 Set gas cylinder regulators to 20 psi.

13.3 Check water level and pressure in the hydrogen generator. The pressure should be

approximately 18 psi.

13.4 Initialize the carbon analyzer operating software. From standby press the Continue button. If the program has been exited, double click on the OCECINST icon.

13.5 Set the gas flows using the needle valves or flow regulators on the analyzer's front panel. Adjust each flow by observing the readout on the flow table and set to the specified range as follows:

| Gas | Flow (cc/min) |
|-----------------|---------------|
| Air | 280 -300 |
| Hydrogen | 42 -46 |
| Helium 1 | 54 - 58 |
| Helium 2 | 12 - 15 |
| Helium 3 | 67 - 70 |
| Helium/Oxygen | 12 - 15 |
| Calibration gas | 10 - 15 |

13.6 Set the H₂ flow to give a rich mixture (60-70 cc/min) and ignite the FID with the butane lighter. Check for ignition by checking the FID exhaust for condensation. Adjust the H₂ flowrate to the correct operating range (42 - 46 cc/min)

13.7 Allow the analyzer to warm up for at least 30 minutes. The back oven temperature should reach 870 °C and the methanator oven should be at the controlled temperature of 500 °C.

13.8 Check for a pressure indication of about 1.20 psi while in the idle state.

13.9 Select the appropriate parameter file. This is a text file containing the temperature profile used to control the OC/EC instrument's temperature ramps. For STN samples, select Quartz_epa.par. Appendix B, figure 2 lists the parameter file used for analysis of STN samples.

13.10 Enter a file name for raw-data input. Raw data for each analysis will append to this text file. An example naming convention for a raw data file follows.

Current date.txt

(example: c:\data\06Sep01.txt for the carbon analytical session acquired on September 6, 2001)

13.11 Run the "Clean Oven" cycle.

13.12 Check all gas flow rates and adjust if necessary.

14.0 Calibration with external standards

- 14.1 Punch out a new, clean 1.5 cm² section of a quartz filter.
- 14.2 Open the quartz door to the oven and place on the wire hanger..
- 14.3 Partially remove the quartz boat from the oven with the silicon covered forceps and place it on the support tray.
- 14.4 Place the punch on the quartz boat and slide the boat in gently until it is stopped by the tip of the thermocouple.
- 14.5 Close the oven door ensuring that the "O" ring seals tightly into the front of the oven and clamp. (Check pressure)
- 14.6 Run the "Clean Oven" cycle to completely clean the filter.
- 14.7 After the "Clean Oven" cycle completes and before the oven door is opened, run an instrument blank by analyzing the cleaned filter punch. Results of the instrument blank analysis should be less than 0.3 ugC/cm².
- 14.8 Open the quartz door to the oven and pull the quartz filter boat containing the cleaned punch to the front of the oven. Use a precision syringe or the Eppendorf pipper to deliver 10.0 uL of the first sucrose standard to the clean filter punch. Push the filter boat into the oven, close the quartz door of the oven and allow the filter to dry inside the oven for 8 - 10 minutes. The laser and pressure should return to approximately the same readings as the they were before the punch was spiked.
- 14.9 Analyze the filter punch as described in Section 16.
- 14.10 Repeat step 14.2 - 14.9 until all standards have been analyzed.

15.0 Internal Standard Calibration

A 5% methane in helium standard is injected automatically through a fixed volume loop at the end of each analysis. Integration of the methane peak area along with the known mass of carbon in the loop is used to calculate an instrument relative response factor for each analysis. The mass of carbon contained in the loop is calculated from the results of the external standards calibration described in Section 14 as follows:

- 15.1 Analyze a series of external sucrose standards as described in section 14.
- 15.2 Reduce the raw data using the OCECalc118 software as described in Section 20 to determine the observed concentration of standard in ugC/cm²
- 15.3 Multiply the observed TC concentration (ug/cm²) of each standard by the punch area (cm²) to convert ug/cm² to total ug carbon.
- 15.4 Compute the least squares correlation coefficient and slope of the computed mass of carbon vs. the actual mass of carbon spiked using a forced origin. The slope must be

≥ 0.95 and the correlation coefficient (r^2) must be ≥ 0.998 . If the r^2 criteria is not met, determine the cause and correct the problem. The multipoint calibration must be repeated and a new r^2 computed. If the slope criteria is not met, a new calibration factor should be computed as follows:

15.4.1 For each standard, determine the ratio of the true concentration to calculated concentration. Ratio = True Value/Observed Value.

15.4.2 Open C:\OCECPAR\CALCPAR.TXT. (Figure 3). Line 2 of the file contains the calibration factor which is used to correlate the methane concentration contained in the methane/helium mix to the instrument's FID response. A new factor is calculated by multiplying the current factor by the average of the ratios determined in 15.4.1. Enter the new factor in line 2 and save the file.

Note: The text file instpar.txt located in C:\ocecpa, contains information that the instrument software uses to control the operating parameters of the instrument. The latest version of instrument control software (209) requires a modification of the instpar.txt file to add new lines of text. See appendix D Figure 4. The additional data included in this file are instrument name, calibration constant and the transit time. These values will be embedded into every raw data text file associated with each analysis. By default, the calculation software (version 118) uses the information imbedded in the raw data to compute carbon concentrations. In order to over-ride the default parameters and use the parameters in the oceccalc.txt file, select the optional check box in the calculation software.

15.4.3 Verify the calibration by running an instrument calibration verification (ICV) standard. If the true value differs more than 10% from the measured value, initiate corrective action to identify and solve any problems with the instrument or standards and repeat the calibration if necessary.

16.0 Running a Routine Sample

16.1 Start the instrument following the procedure given in section 13.

16.2 Check Section 21 for the required quality control samples such as blanks, duplicates and control standards needed for the sample batch.

16.3 The analytical sequence must start, continue, and end with a Continuing Calibration Verification (CCV) standard as follows.

Instrument blank (optional)
CCV
Up to ten sample punches
CCV
Up to ten sample punches
CCV
:
CCV

16.4 Remove the samples for analysis from cold storage and place near the sample work area prepared in Section 12.

16.5 At the computer, set up the base file name under which the raw data for the samples will be stored. A file naming convention is described in Section 13.10. Record the file name in the log book.

16.6 Enter the sample ID, punch size and analyst name into the "Carbon Analysis" screen at the instrument computer. Record the analysis information into the Carbon Analysis Log Book. See appendix A figure 1 for an example of the logbook form.

16.7 Open the sample container. With clean, stainless steel forceps, carefully pick up the filter near its edge and place it on the pre-cleaned aluminum foil work area. Be careful not to disturb the filter deposit. Using the precision punch (cleaned with a new quartz filter), cut out a 1.5 cm² section from the filter.

16.8 Check the "Status" screen to be sure the oven is cool enough to receive a sample.

16.9 Open the quartz door to the oven and place safely on the wire hanger.

16.10 Partially remove the quartz boat from the oven with the silicon covered forceps and place it on the support tray.

16.11 Using the stainless steel forceps, place the punch on the quartz boat and slide the boat in gently until it is stopped by the tip of the thermocouple.

16.12 Close the oven door ensuring that the "O" ring seals tightly into the front of the oven and clamp.

16.13 Check the pressure for a reading of about 1.20 psi. A low pressure indicates a leak at the O-ring sealing the oven door. Record the pressure reading and the laser transmittance in the logbook.

16.14 Press the START ANALYSIS button to begin the analysis. When the analysis has finished, record the FID max reading from the screen display. The FID max must be within 10% of the previous reading. If not, correct the problem (eg. leak at the oven door O-ring) and re-analyze the sample with a second punch from the same filter.

16.15 After the oven has cooled sufficiently, repeat the procedure for the remaining samples.

17.0 Running a non-routine sample

Non routine analysis is necessary when samples contain high carbonate and/or high elemental carbon

17.1 Procedure for Estimating Carbonate Carbon - Carbonate can be recognized by a sharp peak in the thermogram near the end of the first (non-oxidizing) heating cycle of the analysis, typically after almost all of the organic carbon has been volatilized.

17.1.1 The presence of carbonate carbon can be verified through analysis of a second filter punch after acid treatment. Expose a second punch from the sample

filter to hydrogen chloride vapor in a dessicator, petri dish, or similar chamber containing a small amount of concentrated hydrochloric acid for 1 hour. Remove the filter punch from the chamber and allow the acid vapor to volatilize for at least 30 minutes before analyzing it according to Section 16. Disappearance of the carbonate peak confirms the presence of carbonate carbon. Report organic carbon from this analysis, and report carbonate carbon as uncorrected organic carbon from the first analysis minus organic carbon from the second analysis.

17.1.2 If the carbonate is identified as a single peak (e.g., calcium carbonate), the peak can be manually integrated with the Sunset Laboratory OC/EC calculation program according to section 20.4. This approach is most accurate when the amount of organic carbon between the start and end points of the manual integration is small compared to the amount of carbonate carbon

17.2 Procedure for samples with high elemental carbon loadings. - High elemental carbon (EC) loadings are recognized because the samples are black. High EC would not normally be found with the PM_{2.5} samples. High EC ordinarily occurs with samples collected in occupational settings such as mines or when hi vol samplers are used. When a sample with high EC is loaded into the sample oven, the laser light is essentially completely absorbed, making automatic correction for the OC/EC split point impossible.

17.2.1 If the samples are a set (i.e., contain particulate from the same source), analyze the entire set of samples. Ensure that one of the samples in the set has a loading such that the laser absorbance is acceptable for determining the OC/EC split point. This sample normally appears lighter than the others in the set.

17.2.2 Analyze the raw data with the data calculation software according to section 20. Look for a similar thermogram profile across the set. If the profile is essentially identical for all the samples in the set, the samples having a satisfactory automatic OC/EC split point can be used as the basis for assignment of the split point for the heavily loaded samples. Note the split point time. Re-integrate the sample set manually setting the OC/EC split point at the same point throughout the set.

18.0 Calculation of OCX Integration Start Time

18.1 Using a spreadsheet program, open an oc/ec raw data file with comma delimiters.

18.2 Select an empty cell in the first row of acquisition data.

18.3 Insert a formula to convert the thermocouple readings to °C. Copy the formula down the column to the last row of data.

18.4 Find the row number containing first temperature corresponding to ≥ 550 °C. Each row of data represents one second of analysis time, therefore the number of rows to reach ≥ 550 °C plus the transit time for that instrument is the start time for OCX which is also the beginning time for OC peak 4 integration. See Appendix E for an example.

18.5 Open the calcpar.txt file and enter the time for start integration of OC4.

Note: This equation is used to convert temperature from raw data produced from instruments using software previous to version 209. The thermocouple readings are in the column labeled "front_temperature" in raw data file.

$$\text{Temperature} (^{\circ}\text{C}) = \left[\frac{\text{thermocouple reading}}{32767} \right] (1000)$$

Equation for instruments using instrument software version 209.

$$\text{Temperature} (^{\circ}\text{C}) = 0.2063 \times X^3 - 2.7909 \times X^2 + 107.09 \times X - 35955$$

$$\text{where } X = \frac{\text{thermal couple reading}}{3276.7}$$

19.0 Shutdown

19.1 If intending to return to the analyzer within the next few days, click on the standby box. The back oven temperature will be maintained at a lower than normal temperature to increase the heating coil life. Also, the laser will be off and the pressure will be near zero since there is very little flow.

19.2 Set the gas flows as follows:

Air set to off

He/O₂ set to off

Cal set to off

He1, He2, He3 set to trickle flow at 5 -10 cc/min

H₂ leave at normal flow if using H₂ generator, otherwise set to off

19.3 If not intending to use the instrument for several days, choose EXIT from the FILE menu. This will turn off all power to the ovens, causing them to cool off. Turn off all gases except He1 and He3 which should be set to a trickle flow of about 5 - 10 cc/min.

20.0 Calculations

Raw data for each sample is stored as an ascii textfile as described in Section 13.10. The raw data is reduced and final results are calculated by a software program OCECalc118 provided by Sunset Laboratory. The software creates a comma separated variable (csv) file which can be opened in a spreadsheet such as EXCEL to generate a sample results report.

20.1 Start the OCECalc118 program and select the text file to be reduced.

20.2 Click the "Calculate First Sample" button to calculate the first sample. The software will produce a thermogram and data for each sample including calculated concentrations for organic, carbonate, elemental and total carbon. Each sample's calculated data is written to a csv file that is automatically given the same name as the raw data file.

20.3 Review each thermogram for carbonate, absorbance value, and the automatic split point.

20.4 If carbonate carbon is present as a single peak, it may be evaluated by manual integration of the peak. Enter a numeric value for the start and end points of the carbonate peak. (show up as vertical dashed lines on the on-screen thermogram.) Press the Integrate button to display the recalculated thermogram. The program automatically subtracts the carbonate peak area from the initial organic peak area. This approach is most accurate when the amount of organic carbon between the start and end points is small compared to the amount of carbonate carbon in the same region.

20.5 Concentrations of Organic, Carbonate, Elemental, and Total Carbon and OCX. Open the csv file using a spreadsheet program such as EXCEL. Analysis data for each sample will be displayed in the spreadsheet. OCX concentration will be listed in the column labeled as OC4.

20.6 Mass of Organic, Carbonate, Elemental, Total Carbon and OCX on the Filter (ug C) Calculate the mass (m) of the carbon components on the filter by multiplying the concentration (c) of each component (ug C/cm²) by the deposit area (A) of the filter in cm². For a 47 - mm quartz filter sample using a Met One speciation sampler, the exposed portion of the filter is 38.7 mm in diameter and the area of the deposit is 11.76 cm².

$$m = cA$$

$$A = \pi r^2 = (314159) \left[\frac{38.7 \text{ mm} \left(\frac{1 \text{ cm}}{10 \text{ mm}} \right)}{2} \right]^2 = 11.76 \text{ cm}^2$$

20.7 Concentrations of OC, EC, Carbonate, and Total Carbon in Air (ug/m³). - Concentration (ug/m³) of each type of carbon on a filter is calculated by dividing the mass (ug) by the total volume of air sampled (m³).

$$c = \frac{m}{V_{air}}$$

21.0 QUALITY ASSURANCE

21.1 Initial calibration. Run a complete set of calibration standards, following section 14, at least once a week if performing routine analyses. Compute the linear regression of the computed concentration vs. the actual concentration of carbon using a forced origin. If the correlation coefficient (r^2) is not ≥ 0.998 , correct the problem and repeat the calibration.

21.2 No samples may be analyzed until the calibration has been verified by an independent standard (ICV) prepared from a different lot number or source of carbon (e.g. KHP). The concentration of the ICV should be at the midrange of the calibration curve. If the analyte concentration determined for the ICV differs by more than 10% from its expected value, corrective action must be taken to determine the cause and if necessary, a new initial calibration must be established.

21.3 Daily continuing calibration verification standard (CCV). Run a sucrose CCV at the beginning of each sample batch. The measured carbon (ug/cm²) must be within $\pm 5\%$ of the true value. If the CCV does not meet the $\pm 5\%$ criteria, a new calibration must be performed and a new calibration factor computed.

21.4 Run an instrument blank, using a punch from a pre-cleaned quartz fiber filter, at the beginning of each batch. If the blank is above 0.3 ugC/cm², determine if the problem is with the filter or the instrument, and, if necessary, initiate corrective action to identify the problem before analyzing samples.

21.5 Duplicate analyses. Analyze a duplicate sample punch for each batch or 10% of the samples analyzed, whichever is greater. Acceptance criteria for duplicate measurements is dependant on filter loadings. Criteria for carbon loadings ≥ 5 ug/cm² are based on the relative percent difference (RPD) of duplicate measurements. The acceptance criterion for loadings < 5 ug/cm² is based on absolute error (± 0.75 ug/cm²). See table 2 for acceptance criteria.

| Table 2 | |
|---|--------------------------------|
| Total Carbon Concentration Range | Acceptance Criteria |
| Values greater than 10 ug/cm ² | Less than 10% RPD |
| 5 -10 ug/cm ² | Less than 15% RPD |
| Values less than 5 ug/cm ² | Within 0.75 ug/cm ² |

21.6 Internal Standard - If the internal standard area counts or FID Max for any analysis on a given day is not within $\pm 5\%$ of the average response for all samples run that day, then the analysis must be repeated.

21.7 If carbonate carbon is suspected and the manual integration method (Section 17.1) is used to estimate its concentration, run a CaCO₃ standard to verify the location of the carbonate peak in the thermogram. A CaCO₃ standard need only be run once for a given parameter file.

21.8 Samples with carbon concentrations above the highest calibration standard. The linearity of the instrument must re-verified by analyzing a standard higher in concentration than that of the sample. If the response is not linear, ($r^2 < 0.99$), a second, smaller punch (1cm²) from the quartz filter sample must be analyzed.

21.9 The calibration factor must be updated when the calibration gas (CH₄) cylinder is replaced.

21.10 Archive raw data for each day's analytical batch to the network drive \\MTGAPP1\Groups\PM 2_5\Carbon\Raw Data\. Include the raw data text file, the oceccalc.txt file, the thermal profile parameter file the csv file and the instrument parameter file.

21.11 Check the operation of the methanator by analyzing a NIST certified 5% CO₂ in He gas. This can be done by switching the CH₄ 3-way valve to the CO₂ source and analyzing a sample or standard. The area counts of the CO₂ should be within $\pm 10\%$ of the last CH₄ response.

21.12 The transit time for each instrument must be determined in order for the software to be able to compute an accurate OC/EC split point. The transit time can be determined by analyzing a 40 ug/cm² sucrose standard using the transit.par parameter file. This parameter file omits the cooling step between the non-oxidizing to oxidizing mode of the heating profile. This permits very rapid oxidation of the char which in turn causes a rapid response of the laser signal. Open the raw data file in a spreadsheet in order to easily examine the FID and laser readings. Examine the data near the beginning of the oxygen mode. Note the row numbers at which the laser readings and the FID readings begin to increase. The difference in row numbers is the transit time in seconds. The transit time can also be determined by plotting the laser signal and FID signal (See Appendix F, figure 6). The transit time should be checked after any major maintenance is done such as replacing the quartz oven.

22.0 REFERENCES

22.1 Standard Operating Procedures for the Analysis of Organic and Elemental Carbon (OCEC) on Quartz Fiber Filters, Sunset Laboratory, March 8, 1999

22.2 Standard Operating Procedures for the Determination of Organic, Elemental, Carbonate, Total Carbon, and OCX in Particulate Matter Using a Thermal/Optical Carbon Analyzer, Environmental & Industrial Chemistry Department Center for Environmental Measurements and Quality Assurance, Research Triangle Institute, Research Triangle Park, NC

22.3 NIOSH Method 5040, "Elemental Carbon (Diesel Particulate)," NIOSH Manual of Analytical Methods, 4th ed., Cincinnati, Ohio, January 15, 1997

23.0 APPENDIX A

23.1 Appendix A presents the Carbon Analysis Logbook form (see Figure 1), which must be completed to document the analysis of quartz filter punches by TOT.

23.2 Daily information for each analysis by TOT is entered into this logbook. Most of the fields will be self explanatory. Some headings that may not be obvious are as follows:.

23.2.1 Output Raw Data File: The Sunset Labs TOT Carbon Analyzer operating software running on a dedicated PC acquires raw data and stores it on the local hard disk. Use this field to record the pathway and file name where raw data for the instrument output will be stored. Please note that most of the file pathway has already been printed. Only the filename needs completion with a manual entry. The filename created is the operators choice but the conventional method for file naming for this instrument is to use the date of the analysis for the file name. For example raw data for samples acquired on October 6, 2001 would be stored in a file named "6oct01". The pathway to this file would be "C:\data\6oct01".

23.2.2 Parameter File: The parameter file contains the instrument operating parameters that control the temperature ramps during a sample acquisition. This is a text file with the suffix ".par". The current parameter file name is "Quartz_stn.par". This file is located in the "\PAR" sub-directory. ("C:\\PAR").

23.2.3 Standards: This field is used to record the laboratory notebook number of the standards used for calibration and calibration verification.

23.2.4 Comments: These are comments that aren't covered by one of the other fields. Anomalies or trends should be noted here.

Figure 1

| U.S. EPA/NAREL Carbon Analysis by TOT LOGBOOK | | | | |
|---|---------------------------------------|------------------|-----------|----------|
| Analyst | | Standards | | |
| Date | | Std. A | | |
| Back Oven °C | | Std. B | | |
| CH4 Oven Temp °C | | Std. C | | |
| Output Raw Data File | C:\data\ | | | |
| Parameter File | C:\Program Files\ocec instrument\par\ | | | |
| Comments | | | | |
| Sample ID | PSI | Laser | FID 1 Max | Comments |
| | | | | |
| | | | | |
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| | | | | |

Signature _____ Date _____

24.0 Appendix B

24.1 Appendix B presents an example of a parameter file used by the instrument to control the temperature profile when analyzing a sample for the STN network.

Figure 2

```
'Parameters used for PM2.5 STN program
'analyzes for organic and elemental carbon .
'by Robert A. Cary.
'1995 Feb 15: added calibrationO2 mode.
'mode <comma> time <comma> temperature
'@ regimen must end 'Offline' mode.
,
' purge for 10 sec with blower off.
,
Helium, 10, 1
' start ramping the temperature
Helium, 60, 310
Helium, 60, 480
Helium, 60, 615
Helium, 90, 900
' let the oven cool before starting elemental
Helium, 30*, 0
' elemental
Oxygen, 10, 0
Oxygen, 35, 600
Oxygen, 45, 675
Oxygen, 45, 750
Oxygen, 45, 825
Oxygen, 120, 920
CalibrationOx, 30, 1
CalibrationOx, 50, 0
CalibrationHe, 30, 0

' All done!
' this last mode persists until we start a new sample.
' The last entry *must* be "go offline and turn blower on".
Offline, 1, 0
' end.
```

* 30 second oven cool may vary slightly with different instruments.

25.0 Appendix C

25.1 Appendix C presents an example of the text file used by the OCEC calculation software. This file must be named "calcpar.txt" and located in a folder called "ocecpa" on the C:\ drive.

Figure 3

'calcpar.txt

1.50

21.8

16

26

86

146

167

'Above values are

'Punch area, sq cm

'Calibration constant, ug Carbon

'Transit time, seconds

'Start Integration, OC Pk1 (10 + 16)

'Start Integration, OC Pk2 (26 + 60)

'Start Integration, OC Pk3 (86 + 60)

'Start Integration, OC Pk4 (151 + 16 = time to 550°C + 16)

26.0 Appendix D

26.1 Appendix D presents an example of the instrument parameter file used by the OCEC instrument. This file must be named "instpar.txt" and located in a folder called "ocecpa" on the C:\ drive.

Figure 4

| | |
|-------------------------------|--------------------------------|
| 0,0,325.75,-300.01 | 'He1B3, He1B2, He1B1, He1A |
| 0,0,289.13,-262.53 | 'He2B3, He2B2, He2B1, He2A |
| 0,0,356.76,-322.15 | 'He3B3, He3B2, He3B1, He3A |
| 0,0,345.81,-319.42 | 'HydB3, HydB2, HydB1, HydA |
| 0,0,224.59,-204.9 | 'HeOxB3, HeOxB2, HeOxB1, HeOxA |
| 22.641,-72.432,151.64,-95.534 | 'AirB3, AirB2, AirB1, AirA |
| 0,0,289.58,-273.88 | 'CalB3, CalB2, CalB1, CalA |
| 0,0,167.12,124.77 | 'PresB3, PresB2, PresB1, PresA |
| -186 | 'PresZero |
| -404 | 'FIDZero |
| 30 | 'Front Temp Offset |
| 10 | 'Back Temp Offset |
| 300 | 'Meth Temp Offset |
| 0.000457,-0.0315 | 'Pult_m, Pult_b |
| 8201,-0.8416 | 'Tult_m, Tult_e |
| -0.05944,-0.0048,-0.495 | 'Bk_p, Bk_i, Bk_d |
| -0.0528,-0.0148,-1.056 | 'Meth_p, Meth_i, Meth_d |
| 1 | 'ComPrtNum |
| 0.8 | 'PSIG Min warning |
| 0.25 | 'Laser Scale Expansion |
| 120 | 'AC Power Voltage |
| EPA 1 | 'INSTRUMENT NAME |
| 21.8 | 'CAL CONST |
| 16 | 'TRANSIT TIME |

27.0 Appendix E

27.1 Appendix E presents an example of raw data text used for transit time calculation. The first temperature above 550°C occurs at row # 150. If the transit time for this instrument is 8 seconds, then 158 seconds is the start time for the OCX peak integration.

Figure 5

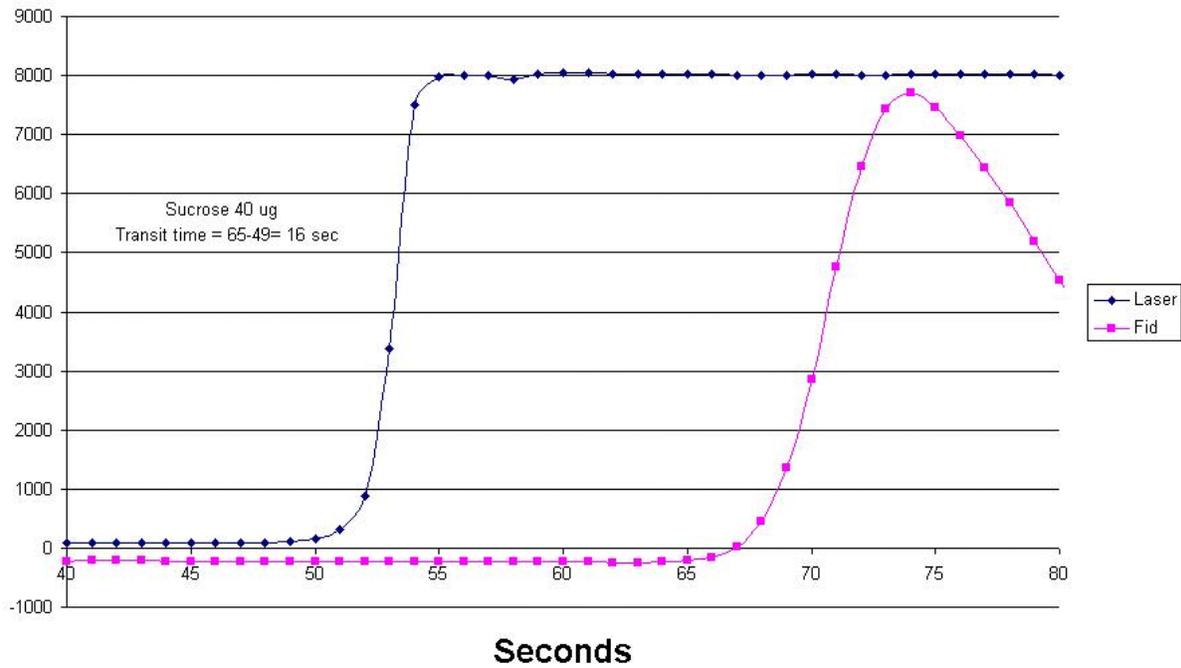
| Row # | FID1 | FID2 | front temp | laser | laserlow | pressure | mode | | Temp deg C |
|-------|------|------|------------|-------|----------|----------|------|--------|------------|
| 1 | 2034 | 4 | 1325 | 16057 | 83 | 16133 | He | 3588 | 39.3 |
| 2 | 2034 | 4 | 1314 | 16050 | 82 | 16132 | He | 3460 | 38.9 |
| 3 | 2034 | 3 | 1346 | 16051 | 84 | 16141 | He | 3332 | 39.9 |
| 4 | 2035 | 4 | 1314 | 16031 | 82 | 16133 | He | 3204 | 38.9 |
| 5 | 2035 | 3 | 1326 | 16051 | 83 | 16137 | He | 3077 | 39.3 |
| 6 | 2035 | 2 | 1320 | 16112 | 83 | 16141 | He | 2948 | 39.1 |
| 7 | 2035 | 4 | 1328 | 16089 | 83 | 16139 | He | 2820 | 39.4 |
| 8 | 2033 | 3 | 1335 | 16178 | 84 | 16140 | He | 2693 | 39.6 |
| 9 | 2035 | 4 | 1317 | 16088 | 83 | 16134 | He | 2564 | 39.0 |
| 10 | 2034 | 3 | 1319 | 16232 | 81 | 16134 | He | 2436 | 39.1 |
| 11 | 2034 | 4 | 1321 | 16058 | 82 | 16135 | He | 2308 | 39.1 |
| 12 | 2033 | 3 | 1331 | 16054 | 83 | 16142 | He | 2181 | 39.5 |
| 13 | 2033 | 4 | 1361 | 16015 | 83 | 16156 | He | 2052 | 40.4 |
| 140 | 2039 | 3 | 16618 | 15685 | 95 | 16452 | He | -14204 | 494.6 |
| 141 | 2039 | 5 | 16724 | 15650 | 98 | 16487 | He | -14332 | 497.7 |
| 142 | 2040 | 5 | 16900 | 15665 | 101 | 16513 | He | -14459 | 502.8 |
| 143 | 2040 | 5 | 17040 | 15660 | 105 | 16537 | He | -14588 | 506.8 |
| 144 | 2040 | 4 | 17223 | 15627 | 109 | 16564 | He | -14716 | 512.1 |
| 145 | 2039 | 4 | 17420 | 15629 | 114 | 16586 | He | -14843 | 517.8 |
| 146 | 2039 | 4 | 17616 | 15601 | 119 | 16606 | He | -14972 | 523.5 |
| 147 | 2040 | 5 | 17834 | 15600 | 123 | 16615 | He | -15100 | 529.8 |
| 148 | 2039 | 5 | 18077 | 15615 | 129 | 16627 | He | -15228 | 536.9 |
| 149 | 2039 | 4 | 18287 | 15621 | 136 | 16642 | He | -15356 | 543.0 |
| 150 | 2039 | 6 | 18579 | 15633 | 143 | 16659 | He | -15484 | 551.5 |
| 151 | 2040 | 4 | 18811 | 15617 | 139 | 16659 | He | -15612 | 558.2 |
| 152 | 2039 | 4 | 18989 | 15617 | 118 | 16656 | He | -15739 | 563.4 |
| 153 | 2039 | 5 | 19202 | 15610 | 112 | 16655 | He | -15868 | 569.6 |
| 154 | 2040 | 5 | 19426 | 15642 | 116 | 16644 | He | -15995 | 576.2 |
| 155 | 2039 | 4 | 19607 | 15631 | 106 | 16624 | He | -16123 | 581.5 |
| 156 | 2040 | 5 | 19771 | 15604 | 100 | 16606 | He | -16252 | 586.3 |
| 157 | 2038 | 5 | 19950 | 15580 | 97 | 16588 | He | -16379 | 591.5 |
| 158 | 2039 | 5 | 20044 | 15570 | 94 | 16553 | He | -16507 | 594.3 |

28.0 Appendix F

28.1 Appendix F presents a graph plotting the FID and laser signals on the Y axis vs. time in seconds on the X axis. The transit time is the number of seconds from where the laser signal first begins to rise to where the FID signal begins to rise. In this case the laser signal begins to rise at 49 seconds and the FID begins at 65 seconds. Therefore the transit time is 16 seconds.

Figure 6

Transit time 11 Nov 02



29.0 Appendix G

29.1 Appendix G presents an example of the carbon analyzer / software user interface with a thermogram of a sucrose standard. (Figure 4)

Figure 7

